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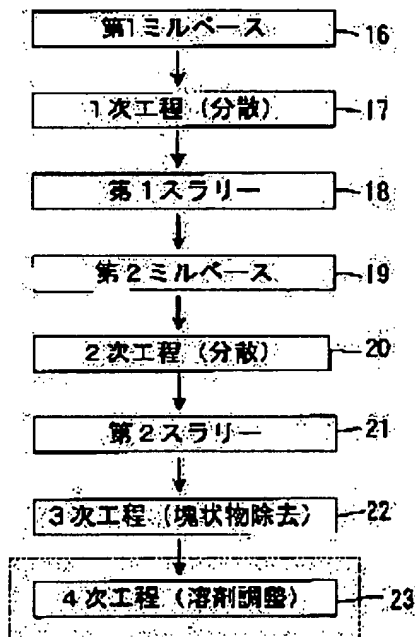
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(54) CONDUCTIVE PASTE FOR PHOTOGRAVURE PRINTING AND ITS PRODUCING  
 METHOD AS WELL AS LAMINATED CERAMIC ELECTRONIC COMPONENT

(57)Abstract:

PROBLEM TO BE SOLVED: To solve the problems that the precipitation of a metallic powder is caused by reducing viscosity for adapting a conductive paste for photogravure printing and stable continuous printing performance at a high speed is precluded by increasing the viscosity.

SOLUTION: A first slurry 18 is obtained by giving mixing and dispersing treatment to a solid component including the metallic powder, a dispersant and a solvent component (a primary process 17). A second slurry 21 is obtained by dispersing a resin component mixed with the solvent component into the first slurry 18 (a secondary process 20). The conductive paste is obtained by removing 1.0  $\mu$ m or larger bulk materials from the second slurry 21 (a tertiary process 22). The conductive past is a thixotropic fluid having a viscosity of 1 Pa.s or more at a shear rate of 0.1 ( $s^{-1}$ ), wherein a viscosity change rate is 50% or more at the shear rate of 10 ( $s^{-1}$ ) with the viscosity at the shear rate of 0.1 ( $s^{-1}$ ) as a criterion.



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**DETAILED DESCRIPTION**

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the laminating ceramic electronic parts constituted by using for formation of the conductive paste suitable for gravure, its manufacture approach, and this conductive paste of the inner conductor film.

[0002]

[Description of the Prior Art] In recent years, to laminating ceramic electronic parts, much more lamination and low cost-ization are desired with the miniaturization of the various electronic equipment which made the portable telephone the example of representation. For example, in the stacked type ceramic condenser, in order to realize large capacity-ization, lamination of the thickness of a dielectric ceramic layer is carried out to 5 micrometers or less, and it is multilayered with 300 or more layers also about the number of laminatings of a dielectric ceramic layer.

[0003] Moreover, when modification into base-metal ingredients, such as nickel and Cu, from noble-metals ingredients, such as Ag and Pd, is made and a conductive paste is used for formation of the inner conductor film as a conductive metallic material used in inner conductor film like the internal electrode for obtaining electrostatic capacity for low-cost-izing, in connection with lamination, detailed-ization of the particle size of the metal powder contained in a conductive paste is also progressing.

[0004] Conventionally, generally in laminating ceramic electronic parts, screen-stencil is used as an approach of forming the inner conductor film by the conductive paste on a ceramic green sheet. However, in long screen-stencil of baton time amount, since productivity is low, efficient-ization of such inner conductor film presswork is desired. It is possible to adopt the gravure approach in which high-speed printing is possible as one of the cures which raise the productivity in inner conductor film presswork.

[0005] In order to form the inner conductor film of laminating ceramic electronic parts by gravure, gravure electrode ink and its manufacture approach are proposed in JP,10-199331,A and JP,10-335167,A.

[0006] The printability in gravure is satisfied in these official reports by considering as the ink which hypoviscosity-ized viscosity of conductive ink to 1 or less Pa-s, and suppressed generating of thixotropy nature unlike the conductive paste used for the conventional screen-stencil. In order for the gravure ink in publication or a package application to also satisfy a version fogging and the printability about an imprint, the viscosity is actually designed by hypoviscosity below 0.5Pa and s.

[0007] Moreover, the manufacture approach of the stacked type ceramic condenser which forms the pattern for inner conductor film by intaglio offset printing is proposed in JP,2000-76930,A.

[0008]

[Problem(s) to be Solved by the Invention] If paste viscosity is made low at below 1Pa and s in order to carry out to gravures, since the conductive paste used for formation of the inner conductor film with which laminating ceramic electronic parts are equipped has the comparatively high content ratio of the metal powder which is an electric conduction component, the fault to which the comparatively large metal powder of specific gravity sediments during a paste is checked. In order to carry out phase splitting of the conductive paste by sedimentation of metal powder, the dispersibility of the metal powder under paste becomes less homogeneous.

[0009] Consequently, the problem which cannot secure the continuation printing nature by which the metal restoration ratio in the thickness of a printing paint film and a paint film was stabilized to the high-speed printing which is dispersion and an advantage in gravure occurs. Moreover, by dispersion in the thickness of a printing paint film, and the metal restoration ratio in a paint film, the degree of sintering of the metal powder

within the inner conductor film changes with locations, therefore dispersion in the effective area of the inner conductor film arises. In the result, for example, a stacked type ceramic condenser, the problem in connection with the electrical characteristics of electronic parts occurs -- the target electrostatic capacity is not obtained. [0010] In order to prevent sedimentation of metal powder, the paste viscosity to which metal powder cannot run is required. However, if viscosity is too high like the conductive paste used for screen-stencil or intaglio offset printing, since poor printing, such as a poor imprint and version plugging, will occur on the other hand, the printing paint film which has homogeneous thickness cannot be obtained. So, though sedimentation of metal powder can be prevented, it is necessary to design paste viscosity which poor printing does not generate at the time of printing.

[0011] Then, the purpose of this invention is offering the conductive paste for gravures which solves the problem of sedimentation of the metal powder mentioned above, and can realize stable gravure fitness in a high speed, and its manufacture approach.

[0012] Other purposes of this invention are offering the laminating ceramic electronic parts constituted by using for formation of the conductive paste mentioned above of the inner conductor film.

[0013]

[Means for Solving the Problem] If this invention is summarized, by using the conductive paste of a thixotropy fluid, the viscosity which can prevent sedimentation of metal powder is held in the state of a low shear rate, by reducing viscosity with the comparatively high shear rate which joins a conductive paste, a fluidity will be raised and the stable continuation printing nature in a high speed will be obtained in gravure at the time of another side and printing.

[0014] This invention is first turned to the conductive paste used in order to form the inner conductor film in laminating ceramic electronic parts equipped with the inner conductor film prolonged in accordance with the specific interface between two or more ceramic layers and a ceramic layer by gravure.

[0015] In order that the conductive paste concerning this invention may solve the technical technical problem mentioned above, 30 - 70% of the weight of the formed element containing metal powder, and 1 - 10% of the weight of a resinous principle, When the viscosity in a shear rate 0.1 (s-1) is the thixotropy fluid of 1 or more Pa-s and is based on the viscosity in a shear rate 0.1 (s-1) including 0.05 - 5% of the weight of a dispersant, and the solvent component as the remainder It is characterized by the viscosity rate of change in a shear rate 10 (s-1) being 50% or more.

[0016] The formed element mentioned above may contain ceramic powder.

[0017] Moreover, as for metal powder, it is desirable that they are the powder containing base metal and the powder which contains nickel or copper more specifically.

[0018] Moreover, as for metal powder, it is desirable that the first [ an average of ] particle size is 0.05 micrometers or more and 0.5 micrometers or less.

[0019] Moreover, as for a resinous principle, it is desirable that weight average molecular weight is 5000 or more.

[0020] As for a dispersant, it is desirable that it is a thing containing an anionic dispersant. In this case, an anionic dispersant is polymerization reagent and it is more desirable that that weight average molecular weight is 4500 or more. What contains the monomer which has a carboxylic acid, a sulfonic acid, a phosphoric acid, or the neutralization salt of one of these as an anionic dispersant is used suitably.

[0021] This invention is turned also to the approach of manufacturing the above conductive pastes again.

[0022] The manufacture approach of the conductive paste concerning this invention In order to solve the technical technical problem mentioned above, the 1st mil base containing a formed element, a dispersant, and a solvent component mixing and by carrying out distributed processing It is characterized by having the primary process which obtains the 1st slurry, the secondary process which obtains the 2nd slurry by carrying out distributed processing of the 2nd mil base which mixed the resinous principle and the solvent component to the 1st slurry, and the 3rd process which removes a massive object 1.0 micrometers or more from the 2nd slurry.

[0023] You may have further the 4th process which adjusts the solvent ratio under conductive paste by removing a part of solvent component after the 3rd process mentioned above.

[0024] Moreover, the 4th process includes preferably the process which carries out evaporation removal of a part of solvent component with the application of either [ at least ] heating or reduced pressure.

[0025] Moreover, as for the viscosity of the 2nd slurry before removing a massive object in the 3rd process, it is desirable to be adjusted to 0.5 or less Pa-s.

[0026] Moreover, as for the 3rd process, it is desirable to include the process from which an opening removes a massive object using the filter which are the more than twice of the first [ an average of ] particle size of metal powder and 20 micrometers or less.

[0027] Moreover, the 3rd process is the pressure of 1.5kg/cm<sup>2</sup>. It is desirable to include the process which removes a massive object by the pressure filtration of the following.

[0028] Moreover, in the 3rd process, two or more steps of multistage filtration is applied preferably.

[0029] In addition, in the 3rd process, when a filter is used, this filter may be a depth type or may be a surface type.

[0030] This invention is turned also to laminating ceramic electronic parts equipped with the inner conductor film prolonged in accordance with the specific interface between further two or more ceramic layers and a ceramic layer. The laminating ceramic electronic parts concerning this invention are characterized by the above-mentioned inner conductor film consisting of a sintered compact which calcinated the conductive paste concerning this invention that was mentioned above, and was obtained.

[0031] These laminating ceramic electronic parts are preferably applied to a stacked type ceramic condenser. In this case, in order to arrange the inner conductor film so that electrostatic capacity may be obtained through a ceramic layer, to be further formed on the outside surface of the layered product constituted by laminating ceramic electronic parts having two or more ceramic layers and to take out electrostatic capacity, it has the external electrode electrically connected to the specific thing of the inner conductor film.

[0032]

[Embodiment of the Invention] Drawing 1 is the sectional view showing in illustration the stacked type ceramic condenser 1 as an example of the laminating ceramic electronic parts constituted using the conductive paste for gravures concerning this invention.

[0033] The stacked type ceramic condenser 1 is equipped with the layered product 2. The layered product 2 is equipped with two or more inner conductor film 4 and 5 formed in accordance with two or more specific interfaces between two or more dielectric ceramic layers 3 by which a laminating is carried out, and two or more dielectric ceramic layers 3, respectively.

[0034] It is formed so that even the outside surface of a layered product 2 may be reached, but the inner conductor film 4 and 5 is arranged by turns so that electrostatic capacity may be obtained for the inner conductor film 4 pulled out by even one end face 6 of a layered product 2, and the inner conductor film 5 pulled out by even the other-end side 7 through the dielectric ceramic layer 3 in the interior of a layered product 2.

[0035] In order to take out above-mentioned electrostatic capacity, it is on the outside surface of a layered product 2, and on an end face 6 and 7, the external electrodes 8 and 9 are formed, respectively so that it may connect with the specific thing of the inner conductor film 4 and 5 electrically. Moreover, on the external electrode 8 and 9, it is it-formed and the 2nd [ it ] plating layer 12 and 13 which consists of solder, tin, etc. is further formed for the 1st plating layer 10 and 11 which consists of nickel, copper, etc. on it, respectively.

[0036] In such a laminating ceramic condenser 1, the inner conductor film 4 and 5 gives a conductive paste which is explained below at a detail by gravure on the ceramic green sheet which should serve as the dielectric ceramic layer 3, and consists of sintered compacts which calcinated this and were obtained.

[0037] While being characterized by a conductive paste containing 30 - 70% of the weight of the formed element containing metal powder, 1 - 10% of the weight of a resinous principle, 0.05 - 5% of the weight of a dispersant, and the solvent component as the remainder It is characterized by for the viscosity in a shear rate 0.1 (s-1) being the thixotropy fluid of 1 or more Pa-s, and the viscosity rate of change in a shear rate 10 (s-1) being 50% or more, when based on the viscosity in a shear rate 0.1 (s-1).

[0038] By forming the inner conductor film with which laminating ceramic electronic parts like the inner conductor film 4 and 5 in the stacked type ceramic condenser 1 shown in drawing 1 are equipped by gravure using such a conductive paste, it can have good productive efficiency and laminating ceramic electronic parts like a stacked type ceramic condenser 1 can be manufactured.

[0039] In addition, the viscosity of a conductive paste shows the viscosity which the measurement method measured with the rotating type measurement-of-viscosity machine by the shear rate control system in the measurement temperature of 25\*\*5 degrees C. The viscosity in the shear rate of arbitration can be measured by using this measuring device.

[0040] In a low shear rate, such as a shear rate 0.1 (s-1), since metal powder with large specific gravity sediments when the viscosity of a conductive paste is low, dispersibility falls. Moreover, the more the first [ an

average of ] particle size of the used metal powder becomes small, the interaction between nickel powder or copper powder becomes strong, and, the more it becomes easy to condense. This becomes more remarkable with nickel powder with magnetism. Consequently, since the condensed powder forms a flocks object and sediments, the dispersibility of a conductive paste is spoiled.

[0041] Therefore, in the conductive paste containing impalpable powder especially the nickel impalpable powder which is easy to condense, or copper impalpable powder, it is necessary to weaken the interaction between metal powder and to prevent condensation as metal powder. Moreover, it is necessary to hold the viscosity which does not make coincidence produce sedimentation of the metal powder by the specific gravity difference.

[0042] In order to weaken the interaction between the metal powder which is electric conduction components and to raise dispersibility, it is necessary to make organic substance components, such as a resinous principle and a dispersant, stick to homogeneity to metal powder. By homogeneous adsorption of an organic substance component, the front face will be in the condition of having been covered by the adsorption layer by the organic substance, and each of metal powder will exist during a conductive paste. So, since each metal powder adjoins through an adsorption layer, it is hard to produce the condensation by the interaction between metal powder, and a flocks object is also hard to be formed.

[0043] Moreover, it is not only hard to produce condensation of metal powder, but in the conductive paste with which the front face of metal powder is covered by the adsorption layer of an organic substance component, the interaction by the adsorption layer of an organic substance component exists. The metal powder covered by the adsorption layer forms the structure connected by network between adjoining metal powder by the interaction of an organic substance component in a low shear rate region. That is, a flow of metal powder will be controlled by formation of the structure through an adsorption layer, consequently the viscosity of a conductive paste becomes high.

[0044] According to the conductive paste which relates to this invention based on such a principle, it becomes possible to secure the viscosity in a low shear rate region highly. Moreover, adsorption of the homogeneous organic substance component on the front face of metal powder can also realize effectiveness of the improvement in dispersibility collectively.

[0045] On the other hand, although the conductive paste concerning this invention forms the structure through an organic substance component in the low shear rate region, if a high shear rate is added at the time of gravure, that network structure object will be destroyed. This is for the interaction between adsorption layers to become weaker as a shear rate becomes high, and finally, the metal powder in a high shear rate region exists during a conductive paste, where mutually-independent is carried out. That is, in a high shear rate region, since the metal powder covered by the adsorption layer can flow without condensing in a conductive paste, a large viscosity down happens and the fluidity of a conductive paste improves.

[0046] Since it is such, in gravure, a printability without faults by version plugging, such as a poor imprint and a blur, is acquired.

[0047] As mentioned above, according to the conductive paste concerning this invention, by making homogeneity adsorb an organic substance component to a metal powder front face, the big viscosity down in a high shear rate region can be combined with viscosity reservation in a low shear rate region, and it can realize. Consequently, the conductive paste which is a thixotropy fluid with a large shear rate dependency is obtained, and the both sides of sedimentation of metal powder, prevention of condensation, and the high-speed printability in gravure can be satisfied.

[0048] In the conductive paste concerning this invention, the viscosity in a shear rate  $0.1 \text{ (s}^{-1}\text{)}$  needs to be the thixotropy fluid of 1 or more Pa-s. Therefore, the viscosity of 1 or more Pa-s is secured with a shear rate  $0.1 \text{ (s}^{-1}\text{)}$  by adsorbing the organic substance component to metal powder, and forming the structure which minded the adsorption layer.

[0049] If the viscosity in a shear rate  $0.1 \text{ (s}^{-1}\text{)}$  becomes under 1Pa and s, phase splitting will be caused in the conductive paste which metal powder with large specific gravity becomes easy to sediment, and homogeneity was made to distribute. Since phase splitting of a conductive paste brings about the thickness of a printing paint film, and dispersion of the metal restoration ratio in a paint film, it cannot obtain the stable continuation printing nature and cannot obtain laminating ceramic electronic parts like the laminating ceramic condenser 1 of high quality as a result.

[0050] Moreover, when the conductive paste concerning this invention is based on the viscosity in a shear rate

0.1 (s-1), the viscosity rate of change in a shear rate 10 (s-1) needs to be 50% or more. In order to acquire a good printability by gravure, sufficient viscosity down in the shear rate at the time of printing is called for. Therefore, the viscosity rate of change in the shear rate 10 (s-1) when being based on the viscosity in a shear rate 0.1 (s-1) is chosen as an index of thixotropy nature that a good printability is acquired, and it is supposed that this viscosity rate of change is 50% or more.

[0051] 50% or more of viscosity rate of change makes it possible to carry out mutually-independent and to make it distribute, without making each metal powder which adsorbed the organic substance component to metal powder at homogeneity, and was made to form the structure in a low shear rate region, and was covered with the adsorption layer in the high shear rate region condense, as mentioned above.

[0052] When viscosity rate of change is less than 50%, since the viscosity down of the conductive paste at the time of printing is not enough, faults, such as a poor imprint and version plugging, occur and good continuation printing nature in a high speed cannot be realized.

[0053] In the conductive paste concerning this invention, the content ratio of the formed element containing metal powder is made into 30 - 70 % of the weight, as mentioned above. By adjusting the ratio of a formed element in this range, it is stabilized and the printing paint film thickness made into the purpose can be obtained.

[0054] When the content ratio of a formed element is less than 30 % of the weight, the consistency of metal powder becomes low too much at the consistency of the formed element in a printing paint film, and a twist specification target. Consequently, speaking of the stacked type ceramic condenser 1 shown in drawing 1, faults, such as an open circuit of the inner conductor film 4 and 5, arise at the time of sintering, and the stacked type ceramic condenser 1 which has the electrical characteristics which dispersion arose in the effective area of the inner conductor film 4 and 5, and were stabilized in it cannot be obtained. Moreover, the fall of the dispersibility by sedimentation of the metal powder with which it becomes difficult with which to obtain the viscosity of 1 or more Pa-s in a shear rate 0.1 (s-1), and it serves as a principal component of a formed element is caused.

[0055] On the other hand, if the content ratio of a formed element exceeds 70 % of the weight, faults, such as dispersion in the printing paint film thickness by version plugging, will occur plentifully at the time of gravure.

[0056] The formed element mentioned above may contain ceramic powder besides metal powder. When the layered product 2 of a raw condition which has the structure which carried out the laminating of the ceramic green sheet which should serve as the inner conductor film 4 and 5 formed with the conductive paste and the dielectric ceramic layer 3 speaking of the stacked type ceramic condenser 1 shown in drawing 1 is calcinated at an elevated temperature, If a difference is in sintering temperature between the metal powder contained in the conductive paste used as the inner conductor film 4 and 5, and the ceramic contained in a ceramic green sheet, since the stress by gap of sintering contraction inside a layered product 2 will occur, peeling, a crack, etc. occur in a layered product 2. These evils can be made hard to produce by including ceramic powder in a formed element.

[0057] As metal powder contained in a formed element, the powder which consists of base metal, such as nickel and copper, especially nickel powder can be used advantageously. Although the metal powder which consists of noble metals, such as silver and palladium, can also be used, it becomes possible by using base-metal powder to manufacture more cheaply laminating ceramic electronic parts like a stacked type ceramic condenser 1 as mentioned above.

[0058] As for the first [ an average of ] particle size of metal powder, it is desirable that it is 0.5 micrometers or less. From now on, to laminating ceramic electronic parts like a stacked type ceramic condenser 1, the further miniaturization and low back-ization will be wanted to progress. Therefore, it is desirable to make as thin as possible thickness of the inner conductor film with which laminating ceramic electronic parts are equipped, and in order to be the lamination of such inner conductor film, it is necessary to make particle size of metal powder small. If first [ an average of ] particle size of metal powder is set to 0.5 micrometers or less, it will become possible to correspond to the lamination of the above inner conductor film enough.

[0059] On the other hand, if the first [ an average of ] particle size of metal powder exceeds 0.5 micrometers, it will become difficult not to obtain a thick kink colander but to fully deal the physical thickness of the inner conductor film with the demand of lamination. However, when the first [ an average of ] particle size of metal powder exceeds 0.5 micrometers, it is possible to use suitably the metal powder which has the first [ an average of ] particle size according to the purpose, and there is no change in the effectiveness acquired by this invention.

[0060] Moreover, the smaller one of the first [ an average of ] particle size of metal powder is desirable. However, there may be an increment in cohesive force, a dispersibility fall, etc. by the interaction between metal powder becoming very strong as a concern matter over the pulverization of metal powder. In order to avoid such concern, as for the first [ an average of ] particle size of metal powder, what is set to 0.05 micrometers or more is desirable.

[0061] In the conductive paste concerning this invention, as mentioned above, the content ratio of a resinous principle is made into 1 - 10 % of the weight.

[0062] The reinforcement of a printing paint film is not enough in the ratio of this resinous principle being less than 1 % of the weight, and the fault by the lack of adhesion or poor blocking occurs. Moreover, since the abundance of the resinous principle to the formed element of a under [ a conductive paste ] decreases, it becomes difficult for a resinous principle to stick to homogeneity to formed element powder like metal powder. Consequently, neither the fall of dispersibility nor condensation of formed element powder can be caused, and the conductive paste which has proper thixotropy nature cannot be obtained.

[0063] On the other hand, if the ratio of a resinous principle increases more than 10 % of the weight, faults, such as a fall of the print quality by version plugging and a drying fall of a solvent component, will occur for a viscosity rise of a conductive paste. Moreover, since the amount of organic substance in a layered product raw [ for obtaining laminating ceramic electronic parts ] increases, the structure defect by the fall of cleaning nature etc. occurs, and the property fall of laminating ceramic electronic parts and the fall of the yield are caused.

[0064] What is necessary is to be able to use suitably cellulose, such as a nitrocellulose, ethyl cellulose, and a carboxymethyl cellulose, acrylic resin and ketone resin, a urea-resin, melamine resin, a polyvinyl butyral, petroleum resin, polyester, an alkyd resin, a polyamide, polyurethane, etc., to choose a thing with a solvent component and compatibility as a resinous principle, for example, and just to use. Moreover, these resin can be used in the combination of an independent or multiple thing.

[0065] Moreover, as for the resinous principle used, it is desirable that weight average molecular weight is 5000 or more. Since adsorption-balking to formed element powder like metal powder advances that weight average molecular weight is less than 5000 in a short-time cycle, adsorbent [ over formed element powder ] becomes less enough. In addition, this problem is not a fatal problem for the conductive paste concerning this invention.

[0066] Moreover, as a resinous principle, what has side chains, such as a hydroxyl group, an amide group, and a carboxyl group, to a terminal is desirable.

[0067] In the conductive paste concerning this invention, the content ratio of a dispersant is made into 0.05 - 5 % of the weight, as mentioned above. Since the addition of a dispersant influences the dispersibility of a conductive paste directly, it is properly used within the limits of the above according to the content ratio of a formed element.

[0068] When the content ratio of a dispersant is less than 0.05 % of the weight, since the amount of adsorption of the dispersant to the front face of formed element powder like metal powder is not enough, dispersibility falls, by condensation of formed element powder, the massive object on a printing paint film increases, and the property of laminating ceramic electronic parts falls.

[0069] On the other hand, if there are more content ratios of a dispersant than 5 % of the weight, since the amount of organic substance in a layered product raw [ for obtaining laminating ceramic electronic parts ] will increase, the structure defect by the fall of cleaning nature etc. occurs, and causes the property fall and yield fall of laminating ceramic electronic parts which were obtained.

[0070] What is necessary is to be able to use a macromolecule type anionic dispersant, to choose a thing with compatibility with a solvent component suitably, and just to use it as a dispersant.

[0071] As an anionic dispersant, there is simple substances, such as polyacrylic acid, polyacrylic ester, polymethacrylic acid, polymethacrylic acid ester, phosphoric ester content resin, a maleic acid, sulfonic-acid content resin, polyoxyalkylene, and acid denaturation amide resin, or a copolymer which consists of combination of the thing of these plurality as an example of representation, and it is desirable that weight average molecular weight is 4500 or more polymerization reagents.

[0072] Since adsorption-balking to formed element powder advances that weight average molecular weight is less than 4500 in a short-time cycle, adsorbent [ over formed element powder ] becomes less enough. In addition, this problem is not a problem fatal to the conductive paste concerning this invention.

[0073] It is thought that the adsorption mechanism to formed element powder like metal powder of a dispersant



is based on an acid-base interaction, and it is thought by the system using an organic solvent that the acid-base interaction based on transfer of an unshared electron pair, i.e., the Lewis theory, is dominant. Loop-formation train tail structure is known as a general adsorption gestalt. When controlling the thixotropy nature of a conductive paste, it is possible to control the interaction of formed element powder by introducing the side-chain structure which spreads in the shape of a tail in the structure of a dispersant on the basis of the functional-group section which sticks to formed element powder.

[0074] For example, physically, by introducing an alkyl group with many chains etc. into the side-chain section, the side chain serves as steric hindrance, and the interaction of formed element powder can be weakened.

[0075] Moreover, it is possible to control extent of the interaction of formed element powder by controlling chemically the hydrogen bond nature of the functional group introduced into the side-chain section.

[0076] In fact, taking into consideration the both sides of the above-mentioned physical operation and a chemical operation about a resinous principle or a dispersant, an ingredient and a content ratio are chosen so that the interaction between formed element powder can be controlled proper.

[0077] Generally, the inorganic oxide powder with which front faces, such as metal powder, such as nickel and copper, or ceramic powder, are rich in reactivity shows the basicity with which the front face was covered by the oxide film or the hydroxylation film by the reaction with the oxygen in air, and moisture. That is, homogeneity can be made to adsorb an organic substance component to the front face of formed element powder by distributing formed element powder in the condition that the organic substance component from which the reaction by electron pair transfer serves as activity to the front face of the formed element powder covered by the oxide film or the hydroxylation film exists.

[0078] As a solvent component contained in the conductive paste concerning this invention, solvents, such as alcohols, a terpene system, a ketone system, an ether system, an ester system, a hydrocarbon system, and a polyhydric-alcohol system, can be used suitably, for example, combining independent or a thing with compatibility two or more. In addition, although this solvent component dissolves the both sides of the resinous principle contained in a conductive paste, and a dispersant, its thing with the property in which the organic substance component in a ceramic green sheet is not dissolved is desirable.

[0079] As for the boiling point of a solvent component, it is desirable that they are 50 degrees C or more and less than 250 degrees C. Since evaporation of a solvent component is too quick at the time of printing etc. when the boiling point is less than 50 degrees C, the stable printability is acquired by neither a viscosity rise of a conductive paste nor condensation of a formed element, but workability, such as printing, falls greatly by it. Drying [ of a printing paint film ] becomes it low that the boiling point of a solvent component is 250 degrees C or more too much, and it becomes impossible on the other hand, to correspond to high-speed printing.

[0080] In the conductive paste concerning this invention, as mentioned above, it is important that homogeneity may be made to adsorb an organic substance component to the front face of formed element powder like metal powder. Therefore, in order to obtain such a conductive paste, it is desirable that the following manufacture approaches are used. It explains with reference to drawing 2.

[0081] First, the 1st mil base 16 containing a formed element, a dispersant, and a solvent component is prepared, mixing and the primary process 17 which carries out distributed processing are carried out for these, and the 1st slurry 18 is obtained.

[0082] Subsequently, the 2nd mil base 19 which mixed the resinous principle and the solvent component to the 1st slurry 18 is produced, the secondary process 20 which carries out distributed processing of these is carried out, and the 2nd slurry 21 is obtained.

[0083] Next, the 3rd process 22 which removes a massive object 1.0 micrometers or more from the 2nd slurry 21 can be carried out, and the conductive paste made into the purpose can be obtained.

[0084] According to the difference in the dispersibility by the paste viscosity demanded in the conductive paste which it is going to obtain, and the metal powder to be used etc., the 4th process 23 which adjusts the solvent ratio under conductive paste may be carried out by removing a part of solvent component after the 3rd process 22 mentioned above.

[0085] For example, when the nickel impalpable powder which is easy to condense is used as metal powder, in order to raise the distributed stability by adsorption of the crack nature of nickel powder, and the organic substance component to a nickel powder front face, and re-condensation prevention, distribution of the mill base was performed more by hypoviscosity, it is [ direction ] desirable and, in such a case, the 4th process 23 is carried out.



[0086] When carrying out the 4th process 23, hypoviscosity-ization of the mill base is attained by carrying out excessive-amount addition of the solvent component beforehand in process of the arbitration in the primary processes [ 3rd ] 17, 20, and 22. Moreover, since slurries 18 or 21 also serve as hypoviscosity, it becomes possible to give a sufficient crack and dispersibility also to the formed element by which whose working efficiency of massive object removal at the 3rd process 22 also improved, in addition pulverization was carried out.

[0087] Thus, when the 4th process 23 is carried out, at this 4th process 23, a part of solvent component contained in a conductive paste is removed, but when a solvent component consists of single components and that part and a solvent component consist of two or more components, some or all of a solvent with the lowest boiling point is removed in it, and it is adjusted to moderate paste viscosity.

[0088] Moreover, when heating, reduced pressure, or these both sides can be applied and productive efficiency is taken into consideration as the removal approach of such a solvent component, for example, it is desirable to use together the both sides of heating and reduced pressure.

[0089] The solvent component which carried out superfluous addition is removed from a conductive paste in the 4th process 23. Although the viscosity of a conductive paste rises according to the amount of removal of a solvent component in that case, good dispersibility can be maintained at a condition [ being maintained ] even if viscosity rises, since the organic substance component has already stuck to formed element powder like metal powder at homogeneity and the distributed condition is also stabilized.

[0090] If the manufacture approach of the conductive paste shown in above-mentioned drawing 2 is adopted, adsorption on the formed element powder front face of a dispersant can be efficiently carried out to homogeneity by carrying out distributed processing of a formed element and the dispersant at the primary process 17.

[0091] In the primary process 17, in order to make a dispersant stick to a formed element powder front face preferentially, when adding a resinous principle first here, as for the addition of a resinous principle, it is desirable to carry out to 1/3 or less [ of the total content of the resinous principle in the design presentation ratio of a conductive paste ].

[0092] Thus, in the primary process 17, since homogeneity is made to adsorb a resinous principle efficiently further to a formed element powder front face depending on a dispersant and the case, it is stabilized by the organic substance component, a formed element powder front face can be covered, and the condensation by the interaction between formed element powder can be prevented. Moreover, since the structure which minded the adsorption layer of formed element powder in the low shear rate region is formed of this homogeneous adsorption layer, the paste viscosity in a low shear rate region can be raised.

[0093] Next, although a resinous principle is added to the 1st slurry 18 with a solvent component and distributed processing is carried out to it at the secondary process 20, since the dispersant has already stuck to the front face of formed element powder in the primary process 17, the compatibility of a resinous principle and a formed element is good, and can form in the front face of formed element powder the adsorption layer stabilized further.

[0094] It is the important process in which these primary secondary processes 17 and 20 influence the fluid characteristic of the conductive paste concerning this invention, and by formation of a stable adsorption layer, the interaction between formed element powder can be weakened and the conductive paste in which the comparatively large thixotropy nature of the viscosity rate of change by the shear rate is shown can be obtained.

[0095] The disperser suitable for distribution of the hypoviscosity mill base can be suitably used for distributed processing carried out in each of the primary secondary processes 17 and 20. As a disperser which can be used, an impeller disperser, a homogenizer disperser, a pot disperser, a sand mill disperser, etc. are mentioned, for example. In addition, generally, although the same disperser is used in the primary process 17 and the secondary process 20, a different disperser may be used in consideration of the productivity and the property of the viscosity of the mill base which should be distributed, and a disperser.

[0096] As a formed element, various powder may be used like inorganic oxide powder, such as metal powder, its alloy powder, and a ceramic. When such, the optimal dispersant and a slurry presentation may differ from distributed conditions etc. about each powder.

[0097] By mixing two or more slurries obtained by carrying out distributed processing under the optimal dispersant, a slurry presentation, distributed conditions, etc. about each powder, when above It may be made to

obtain the 1st slurry 18 or the 2nd slurry 21, and after removing a dilution solvent from two or more 2nd slurries 21 and obtaining two or more middle pastes, these are mixed and you may make it obtain the conductive paste of the last presentation made into the purpose.

[0098] Moreover, at the 3rd process 22, as mentioned above, the massive object (projection which appears in a printing side) which exists in the 2nd slurry 21 is removed. It has become clear by analysis that this massive object consists of a non-melt of organic substance components, such as the foreign matter and resinous principle which are mixed in the process of one of the non-distributed objects of the formed element powder contained in the 2nd slurry 21, and a dispersant, etc. If the inner conductor film is formed with the conductive paste in the condition that such a massive object was included, in order for this massive object to cause the problem of piercing through a ceramic green sheet and reducing remarkably the dependability and the yield of laminating ceramic electronic parts which were obtained, with the laminating ceramic electronic parts to which lamination progresses, it is necessary to remove in the manufacture process of a conductive paste.

[0099] As for the viscosity of the 2nd slurry 21 before removing a massive object in this 3rd process 22, it is desirable to adjust to 0.5 or less Pa-s. Viscosity here shows the viscosity measured with the rotating type measurement-of-viscosity machine on condition that the measurement temperature of 25\*\*5 degrees C, and a shear rate 10 (s-1).

[0100] Since the differential pressure at the time of passing a fine filter as it is the viscosity to which the 2nd slurry 21 exceeds 0.5 Pa-s becomes large, filtration time amount becomes long and productivity is usually reduced. By hypoviscosity-izing the 2nd slurry 21, the filtration time amount in the 3rd process 22 as a massive object removal process can be shortened, and productive efficiency can be raised.

[0101] Hypoviscosity-izing of the 2nd slurry 21 is possible by warming of the 2nd slurry 21, or the solvent addition to the 2nd slurry 21. For example, it is desirable to warm the 2nd slurry 21, in not carrying out the 4th process 23, and when carrying out the 4th process 23, one side or the both sides of warming of the 2nd slurry 21 and solvent addition can be applied. Moreover, as mentioned above, when carrying out the 4th process 23, not only in the preceding paragraph story of the 3rd process 22 as a massive object removal process but in the primary process 17 or the secondary process 20, hypoviscosity-ization of the 2nd slurry 21 may be attained by adding the solvent of an excessive amount from the design value to the mill bases 16 or 19.

[0102] The massive object removal included in the 2nd slurry 21 carried out in the 3rd process 22 uses the filter whose openings are the more than twice of the first [ an average of ] particle size of the metal powder contained in a conductive paste, and 20 micrometers or less, and is the pressure of 1.5kg/cm<sup>2</sup>. It is desirable to carry out by the pressure filtration of the following.

[0103] As long as the filtration accuracy of the filter used is high, the thing of what kind of configuration is sufficient as it. Filters, such as a cartridge-type and a capsule type, are suitable in respect of the filtration accuracy and the ease of use.

[0104] The pressure at the time of filtration is 1.5kg/cm<sup>2</sup>. If it sets up highly with the above, filtration time amount can be shortened, but in order that even a gel organic substance component may pass a filter, use in the low differential pressure condition which made filtration pressure low as much as possible also from the point of a filtration accuracy is desirable. Since it can filter in the state of a hypoviscosity slurry by the manufacture approach of the conductive paste concerning this invention, it is 1.5kg/cm<sup>2</sup>. Even if it is the pressurization of the following, a slurry can be filtered with good productive efficiency. Therefore, what is necessary is for slurry viscosity just to adjust filtration pressure suitably.

[0105] If this exceeds 20 micrometers about the opening of the filter used in the 3rd process 22, the amount of loss of metal powder will decrease, but since coarse grain is not removed, a massive object remains during a conductive paste. Therefore, the purpose of massive object removal at the 3rd process 22 is not attained.

[0106] Moreover, it is effective for the filter for removing the smallest massive object to use the filter which has a twice as many opening as the first [ an average of ] particle size of the metal powder contained in a conductive paste. For example, when using the metal powder whose first [ an average of ] particle size is 0.2 micrometers, it is effective to use the filter whose opening is 0.4 micrometers. Usually, metal powder has the particle size distribution of the width of face of arbitration. Therefore, since most metal components will be substantially removed with the filter of the same opening with the first [ an average of ] particle size in almost all cases, it is not desirable.

[0107] Any of the surface type which used depth types, such as a spool type which involved in the cotton fiber and the glass fiber, or the membrane type of polytetrafluoroethylene, the nonwoven fabric of polypropylene,

etc. as a class of filter are sufficient. What is necessary is just to choose suitably the quality of the material and structure of the filter which should take into consideration the resistance over the solvent used in manufacture of a conductive paste etc., and should be used.

[0108] When removing a deforming impurity like gel resin out of the paste by which filtration processing is carried out, it is desirable to use a filter depth type [, such as a spool type, ].

[0109] Moreover, it is desirable to use a filter surface type [, such as a high membrane type of a filtration accuracy, ], for example, in manufacturing the conductive paste used in order that the thickness of the ceramic green sheet which should serve as the dielectric ceramic layer 3 like a stacked type ceramic condenser 1 may form the inner conductor film in a thin situation. Moreover, a higher filtration accuracy can be attained also by using it combining each filter surface type [, such as depth types, such as a spool type, and a membrane type, ].

[0110] If filtration with such a precision filter is performed, a certain amount of formed element will be removed. Usually, the conductive paste is adjusting the spreading thickness at the time of the film formation by printing etc. with the content of a formed element. Therefore, if the content of a formed element falls from a design value as a result of filtration, the problem that the spreading thickness made into the purpose cannot be obtained will occur.

[0111] Then, a gap of the formed element content of the obtained conductive paste can be prevented by setting up more highly the formed element content under paste before filtration from a design value, and foreseeing loss of the formed element by filtration.

[0112] Moreover, when changing loss of the formed element by filtration for every lot, it is also possible to adjust a formed element content by adding the main solvent contained in a conductive paste so that the formed element may be added more highly about 3 to 4% and it may become the formed element content made into the purpose after filtration from the amount of loss of the formed element by the usual filtration.

[0113] For massive object removal, when condensation of formed element powder is strong, or when an opening uses a fine filter 20 micrometers or less, and there are many impurities, plugging occurs in a filter and the life of a filter may fall to it extremely.

[0114] In order to avoid such a problem, it is desirable to apply multistage filtration using two or more steps of filters. As for a multistage filter, at this time, it is desirable that openings differ mutually. And from the filter which gives the filtration accuracy made into the last purpose, if a filter coarser than the filtration accuracy made into the purpose is arranged at least one step in the preceding paragraph, while a filtration efficiency will improve in it, loss of a formed element can also be controlled in it to the minimum, and the life of the filter of the last stage can also be developed in it.

[0115] What is necessary is to be able to apply gas feeding by liquid transport with pumps, such as a diaphragm pump, a Viking pump, a tube pump, and a MONO pump, the compressed air, nitrogen gas, etc. as a liquid transport method of the 2nd slurry 21 to a filter, and just to choose suitably in the range which does not exceed setting pressure-proofing of a filter.

[0116] As mentioned above, according to the manufacture approach of the conductive paste concerning this invention, homogeneity can be made to be able to adsorb an organic substance component on a formed element powder front face efficiently, and formed element powder can be distributed good. Consequently, it is high quality and the conductive paste concerning this invention which is the thixotropy fluid in which a big shear rate dependency is shown can be manufactured stably.

[0117]

[Example(s) of Experiment] Next, the example of an experiment carried out according to this invention is explained. In this example of an experiment, the conductive paste for gravures was used in order to form the inner conductor film of a stacked type ceramic condenser.

[0118] First, the conductive paste concerning each of the samples 1-26 as shown in Table 1 was produced. In Table 1 and 2 mentioned later, this invention of the sample by which \* is given to the sample number is out of range.

[0119] With reference to Table 1, the numeric value indicated by each column of a "ratio" shows the weight rate of each component when making the obtained conductive paste into 100 % of the weight by weight %.

[0120] Moreover, the numeric value of the right-hand side in the column of the "component" of "a formed element 1" shows the first [ an average of ] particle size (micrometer) of the nickel powder used as formed element powder, and copper powder.

[0121] In addition, the "dielectric powder" in the column of the "component" of "a formed element 2" is

BaTiO<sub>3</sub> system dielectric ceramic powder, and what has the first [ an average of ] particle size of 0.2 micrometers was used for it in this example of an experiment.

[0122] Moreover, except for a sample 15, weight average molecular weight is 5000-250000, and the weight average molecular weight of the "denaturation cellulose" shown in the column of the "component" of a "resinous principle" is 2800 only about a sample 15.

[0123] Moreover, except for a sample 20, weight average molecular weight is 4500-200000, and the weight average molecular weight of the "denaturation polyacrylic ester" in the column of the "component" of a "dispersant" is 3500 only about a sample 20. Moreover, the weight average molecular weight of each "maleic-anhydride polystyrene copolymer" is 4500-200000.

[0124] Moreover, that it is in the column of the "paste manufacture approach" with "1" produced the conductive paste concerning a sample according to the following manufacture approaches.

[0125] That is, by mixing a formed element, a dispersant, a resinous principle (it being about 1/3 to a total addition), and a solvent component, the 1st mil base was obtained and this was prepared in the resin pot with a volume of 1l. with the ball (diameter of 5mm). By rotating this prepared pot with fixed rotational speed for 12 hours, pot mill distributed processing was performed and the 1st slurry was obtained.

[0126] Next, by adding the organic vehicle which mixed the resinous principle (residue) and the solvent component beforehand, by obtaining the 2nd mil base and making it rotate with constant speed further for 12 hours, pot mill distributed processing was performed and the 2nd slurry was obtained in the above-mentioned pot.

[0127] Next, after adjusting so that slurry viscosity may become 0.5 or less Pa-s, where the 2nd slurry is warmed, an opening uses the membrane type filter of a twice as many opening as the first [ an average of ] particle size of metal powder (formed element 1) for 20 micrometers, 10 micrometers, 5 micrometers, 3 micrometers, and the last stage, and it is the pressure of 1.2kg/cm<sup>2</sup>. Filtration processing was performed and the conductive paste was obtained.

[0128] on the other hand, "it being "2 to the column of paste manufacture approach"" -- about a certain sample, the conductive paste concerning each sample was manufactured according to the following manufacture approaches.

[0129] That is, by mixing a formed element, a dispersant, a resinous principle (it being about 1/3 to a total addition), and a solvent component, the 1st mil base was obtained and this was prepared in the resin pot with a volume of 1l. with the ball (diameter of 5mm). By rotating this prepared pot with fixed rotational speed for 12 hours, pot mill distributed processing was performed and the 1st slurry was obtained.

[0130] Next, by adding the organic vehicle which mixed the resinous principle (residue) and the solvent component beforehand in the above-mentioned pot, and rotating this with fixed rotational speed for 12 hours, after obtaining the 2nd mil base adjusted so that slurry viscosity might become 0.5 or less Pa-s by adding a solvent component further, pot mill distributed processing was performed and the 2nd slurry was obtained.

[0131] Next, where the 2nd slurry is warmed, an opening uses the membrane type filter of a twice as many opening as the first [ an average of ] particle size of metal powder (formed element 1) for 20 micrometers, 10 micrometers, 5 micrometers, 3 micrometers, and the last stage, and it is the pressure of 1.2kg/cm<sup>2</sup>. Filtration processing was performed and the 3rd slurry was obtained.

[0132] Next, vacuum distillation was carried out so that the 3rd slurry might be heated at 45 degrees C under reduced pressure of 2x10<sup>-2</sup>MPa and some solvents might be removed, and the conductive paste concerning each sample was obtained.

[0133] In addition, about the sample 24, in addition to the toluene and terpeneol which were shown in Table 1, the methanol was added to each of the 1st mil base and the 2nd mil base as a solvent component, and the boiling point removed the whole quantity of the lowest methanol in the process which removes some solvents from the 3rd slurry.

[0134] Moreover, the example of a comparison of this invention is in the column of the "paste manufacture approach" with "package mixing", and after mixing at once, it distributes all of a formed element, a resinous principle, a dispersant, and a solvent component using a ball mill and attritor, it makes it scour each other, and produces the conductive paste concerning each sample.

[0135]

[Table 1]

試料 番号	固形成分1			固形成分2			樹脂成分		分散剤		溶剤成分		ペースト 製造方法
	成分	比率		成分	比率		成分	比率	成分	比率	成分	比率	
* 1	Ni	0.5	20	-	-	-	変性セルロース	5.0	変性ホリブアクリル酸 エステル	1.5	トルエン/ タービネオール	残	2
2	Ni	0.5	30	-	-	-	変性セルロース	5.0		1.5		残	
3	Ni	0.5	40	誘電体粉末	3.6	-	変性セルロース	5.0		1.5		残	
4	Ni	0.5	50	誘電体粉末	5.0	-	変性セルロース	5.0		1.5		残	
5	Cu	0.5	50	誘電体粉末	5.0	-	変性セルロース	5.0		1.5		残	
6	Ni	0.5	65	-	-	-	変性セルロース	5.0		1.5		残	
* 7	Ni	0.5	75	-	-	-	変性セルロース	5.0		1.5		残	
* 8	Ni	0.03	40	-	-	-	変性セルロース	5.0		1.5		残	
9	Ni	0.05	40	-	-	-	変性セルロース	5.0		1.5		残	
10	Ni	0.1	40	-	-	-	変性セルロース	5.0		1.5		残	
11	Ni	0.8	40	-	-	-	変性セルロース	5.0		1.5		残	
* 12	Ni	0.2	50	-	-	-	変性セルロース	0.5		1.5		残	
13	Ni	0.2	50	-	-	-	変性セルロース	1.0		1.5		残	
14	Ni	0.2	50	誘電体粉末	5.0	-	変性セルロース	5.0		1.5		残	
15	Ni	0.2	50	誘電体粉末	5.0	-	変性セルロース	5.0		1.5		残	
16	Ni	0.2	50	-	-	-	変性セルロース	10.0		1.5		残	
* 17	Ni	0.2	50	-	-	-	変性セルロース	12.0		1.5		残	
* 18	Ni	0.2	50	-	-	-	変性セルロース	5.0	-	-		残	
19	Ni	0.2	50	誘電体粉末	5.0	-	変性セルロース	7.0	変性ホリブアクリル酸 エステル	0.05		残	
20	Ni	0.2	50	誘電体粉末	5.0	-	変性セルロース	7.0		0.05		残	
21	Ni	0.2	50	-	-	-	変性セルロース	7.0	無水マレイン酸 ポリスチレン共重合体	5		残	
22	Ni	0.2	50	-	-	-	変性セルロース	3.0		3	トルエン	残	1
23	Ni	0.2	50	-	-	-	変性セルロース	3.0		3	トルエン/ タービネオール	残	2
24	Ni	0.2	50	-	-	-	変性セルロース	3.0		3	タービネオール	残	
* 25	Ni	0.2	50	誘電体粉末	4.5	-	変性セルロース	3.0		3	トルエン/ 2-プロパノール	残	一括混合
* 26	Ni	0.2	50	-	-	-	変性セルロース	3.0		3	2-プロパノール	残	

[0136] Next, evaluation about each item as shown in Table 2 was performed about the conductive paste concerning each sample shown in Table 1. In addition, about a sample 8, since the nickel powder as a formed element 1 was condensing very strongly, the evaluation was not performed.

[0137] In the detail, viscosity when the shear rate of 0.1 (s-1) and 10 (s-1) is added was measured more under the 25\*\*5-degree C environment about the conductive paste concerning each sample with the rotating type measurement-of-viscosity machine of a shear rate control system. The result is shown in the column of "viscosity" of Table 2.

[0138] Moreover, based on the formula of viscosity rate-of-change (%) =  $\{(\text{viscosity in shear rate } 0.1\text{-s-1}) - (\text{viscosity in shear rate } 10\text{-s-1})\} / (\text{viscosity in shear rate } 0.1\text{-s-1}) \times 100$ , it asked for viscosity rate of change from the measurement result of above-mentioned "viscosity." The result is shown in the column of the "viscosity rate of change" of Table 2.

[0139] Moreover, in order to check the sedimentation condition of a formed element, after putting the conductive paste immediately after production in the test tube and leaving it for 24 hours with a quiescent state, viewing estimated the sedimentation degree of formed element powder (nickel powder or copper powder). The result is shown in the column of "sedimentation of formed element powder" in Table 2, it is shown that sedimentation did not produce "O" substantially, it is shown that sedimentation produced "\*\*\*" a little, and it is shown that comparatively many sedimentation produced "x."

[0140] Moreover, it evaluated as follows about the gravure fitness of the conductive paste concerning each sample.

[0141] First, the ceramic green sheet with a thickness of 5.0 micrometers was fabricated on the film which consists of polyethylene terephthalate. Moreover, the gravure version of a configuration with which thousands of chip patterns are obtained in printing area was used for the printing cylinder for gravures at gravure using the photogravure printing machine used for a commercial package material application.

[0142] next, the conductor made into the purpose on an above-mentioned ceramic green sheet -- applying the predetermined printing conditions that film thickness is set to 1.5 micrometers, continuation printing of the conductive paste concerning each sample was carried out, and the 20m [/second] print speed estimated the thickness of the printing paint film after carrying out continuation printing for 2 hours, the existence of a flake, and the existence of a massive object.

[0143] In addition, these evaluations were performed about 50 points of the arbitration in printing area, fluorescence X rays performed thickness and the metaloscope performed observation of a flake and a massive

object.

[0144] These results are shown in each column of "printing paint film thickness", "the existence of a flake", and "the existence of a massive object" in Table 2.

[0145] Next, after carrying out the laminating of the predetermined number of sheets after drying the ceramic green sheet which printed the conductive paste and pressurizing it on condition that predetermined, it cut into the predetermined dimension and the raw layered product for the stacked type ceramic condenser which makes electrostatic capacity of 100nF a design value was obtained. Next, the raw layered product was calcinated at predetermined temperature, the external electrode was further formed by baking, and the stacked type ceramic condenser used as a sample was obtained.

[0146] Thus, the electrostatic capacity of the obtained stacked type ceramic condenser was calculated. The result is shown in "electrostatic capacity" in Table 2 at the column.

[0147] In addition, about the sample 5 using copper powder as metal powder, since processing on the same baking conditions as other samples which used nickel was impossible, processing to a layered product was not performed but it stopped from printing to gestalt observation evaluation of the paint film on the ceramic green sheet after desiccation.

[0148]

[Table 2]

試料 番号	粘度(Pa·S)		粘度 変化率 (%)	固形成分 粉末の沈降	印刷塗膜 厚み ( $\mu\text{m}$ )	白点 の有無	塊状物 の有無	静電 容量 (nF)	判定
	$0.1\text{s}^{-1}$	$10\text{s}^{-1}$							
* 1	1.0	0.4	60	$\Delta$	1.17	有	無	87	$\times$
2	1.4	0.4	71	$\bigcirc$	1.52	無	無	101	$\bigcirc$
3	1.8	0.5	69	$\bigcirc$	1.49	無	無	100	$\bigcirc$
4	1.8	0.6	87	$\bigcirc$	1.51	無	無	100	$\bigcirc$
5	1.8	0.5	72	$\bigcirc$	1.50	無	無	-	$\bigcirc$
6	2.4	0.8	67	$\bigcirc$	1.48	無	無	98	$\bigcirc$
* 7	3.6	1.8	50	$\bigcirc$	1.25	有	無	85	$\times$
* 8	凝集	凝集	-	-	-	-	-	-	$\times$
9	3.1	0.8	74	$\bigcirc$	1.52	無	無	103	$\bigcirc$
10	1.6	0.4	75	$\bigcirc$	1.51	無	無	102	$\bigcirc$
11	1.8	0.6	67	$\bigcirc$	1.61	無	無	101	$\Delta$
* 12	1.7	1.0	41	$\bigcirc$	1.27	有	無	80	$\times$
13	1.7	0.5	71	$\bigcirc$	1.48	無	無	99	$\bigcirc$
14	1.7	0.6	65	$\bigcirc$	1.49	無	無	98	$\bigcirc$
15	1.6	0.7	56	$\bigcirc$	1.24	無	無	97	$\bigcirc$
16	2.1	0.7	67	$\bigcirc$	1.52	無	無	102	$\bigcirc$
* 17	2.6	1.4	46	$\bigcirc$	1.39	有	無	83	$\times$
* 18	3.1	1.8	42	$\bigcirc$	1.23	有	有	81	$\times$
19	1.5	0.3	80	$\bigcirc$	1.50	無	無	100	$\bigcirc$
20	1.6	0.8	50	$\bigcirc$	1.50	無	無	98	$\bigcirc$
21	1.4	0.4	71	$\bigcirc$	1.48	無	無	99	$\bigcirc$
22	1.7	0.5	71	$\bigcirc$	1.53	無	無	102	$\bigcirc$
23	1.9	0.6	68	$\bigcirc$	1.49	無	無	102	$\bigcirc$
24	1.7	0.4	76	$\bigcirc$	1.51	無	無	101	$\bigcirc$
* 25	0.4	0.1	75	$\times$	1.06	有	無	66	$\times$
* 26	0.3	0.1	67	$\times$	1.00	有	無	61	$\times$

[0149] First, a formed element ratio compares about mutually different samples 1-7.

[0150] Also in which sample, the viscosity in a shear rate  $0.1\text{ (s}^{-1}\text{)}$  was 1.0 or more Pa-s, and viscosity rate of change was also 50% or more. Moreover, although it did not generate at all about samples 2-7 but sedimentation of formed element powder was also generated a little about the sample 1, there was especially no problem.

[0151] however, a formed element with this invention out of range -- 20% of the weight of the sample 1 -- and similarly by 75% of the weight of the sample 7, fault was checked by a printability and electrostatic capacity.

[0152] That is, by the sample 1, since there were few content ratios of the nickel powder as a formed element, sufficient printing paint film thickness was not able to be obtained. Moreover, the flake occurred by the poor imprint in which sedimentation of nickel powder participated. In addition, since the nickel powder consistency in a printing paint film was low, the effective area of the inner conductor film after baking fell, and sufficient electrostatic capacity was not obtained.

[0153] Moreover, the stable printing paint film thickness was not obtained by version plugging by the sample 7

with many formed elements. Consequently, the consistency of the nickel powder as formed element powder became low, and the effective area of the inner conductor film after baking decreased, therefore sufficient electrostatic capacity was not obtained.

[0154] sample 2- which has a formed element in 30 - 70% of the weight of the range to these -- also in any of gravure fitness and the electrical characteristics of a stacked type ceramic condenser, it is normal and excelled in 4 and 6.

[0155] Furthermore, it turned out that it is satisfactory also in evaluation [ which / of generating of printing paint film thickness and a flake, and generating of a massive object ], and good gravure fitness is shown from the paste presentation of a sample 4 also about the sample 5 which changed metal powder into copper powder. In this example of an experiment, although electrical-characteristics evaluation as a stacked type ceramic condenser is omitted about the sample 5, if ceramic presentation and the baking conditions of having been suitable for the copper electrode are applied, it can be guessed that the fault which considers especially a printing paint film configuration as a cause is what is not generated.

[0156] Next, the first [ an average of ] particle size of a formed element 1 compares about mutually different samples 8-11.

[0157] The viscosity in a shear rate 0.1 (s-1) was 1.0 or more Pa-s, and the viscosity rate of change of samples 9-11 other than sample 8 was also 50% or more. Moreover, sedimentation of the nickel powder as formed element powder was not generated, either.

[0158] Although 0.03-micrometer nickel powder with the first [ an average of ] particle size smaller than 0.05 micrometers was used by the sample 8, since the interaction between powder was very strong and nickel powder condensed with the magnetism of nickel, homogeneous dispersibility was not acquired but it was difficult to paste.

[0159] On the other hand, by samples 9-11, the first [ an average of ] particle size of nickel powder is 0.05 micrometers or more, and the result which is satisfactory at all was obtained about gravure fitness and the electrical characteristics of a stacked type ceramic condenser. In addition, by the sample 11 using the nickel powder whose first [ an average of ] particle size is 0.8 micrometers, printing paint film thickness increased about 10% as compared with the samples 9 and 10 whose first [ an average of ] particle size of nickel powder is 0.05 micrometers or more and 0.5 micrometers or less. This is because the first [ an average of ] particle size of the used nickel powder is large.

[0160] Under the conditions in this experiment, when the lamination in a stacked type ceramic condenser needs to progress and thickness of a printing paint film needs to be made thin although the result fully satisfied about gravure fitness and the electrical characteristics of a stacked type ceramic condenser is obtained even if it is a sample 11, it is desirable like samples 9 and 10 that the first [ an average of ] particle size of the nickel powder used is 0.05 micrometers or more and 0.5 micrometers or less.

[0161] Next, a resinous principle ratio compares about mutually different samples 12-17.

[0162] Although any sample of the viscosity in a shear rate 0.1 (s-1) was 1.0 or more Pa-s, the viscosity rate of change only of samples 12 and 17 was less than 50%.

[0163] By the sample 12, since the content ratio of a resinous principle was as low as 0.5 % of the weight, the adsorption of a resinous principle to nickel powder did not fully arise, consequently dispersibility fell, and the viscosity rate of change in a high shear rate region became small. In addition, since the resinous principle in a printing paint film also decreased, paint film reinforcement was weak and blocking nature was very bad.

[0164] Moreover, by the sample 17, since there are many content ratios of a resinous principle as 12 % of the weight, the resinous principle which dissolved and spread in the solvent becomes entangled mutually. Consequently, although the dispersibility of nickel powder was maintainable good, the rate of a viscosity down became low.

[0165] For these reasons, sufficient printing paint film thickness was not able to be obtained according to faults, such as version plugging at the time of printing, by the samples 12 and 17 with low viscosity rate of change. Moreover, the flake by poor imprint was also generated and sufficient electrostatic capacity was not obtained by the effective-area fall of the inner conductor film.

[0166] By the sample 15, weight average molecular weight uses [ weight average molecular weight ] 5000 or more resinous principles by samples 13, 14, and 16 as mentioned above to these using less than 5000 resinous principle among the samples 13-16 whose content ratios of a resinous principle are 1 - 10 % of the weight.

[0167] Therefore, since stability and sufficient adsorption are not obtained to formed element powder as



compared with samples 13, 14, and 16, as for the sample 15, viscosity rate of change is small. Even if it is a sample 15, under the conditions adopted in this experiment, the printing property that it is satisfactory practically is acquired, but in order to realize the printability by which high quality was stabilized more, it is desirable to make weight average molecular weight of the resinous principle used or more into 5000 like samples 13, 14, and 16.

[0168] Next, the content ratio of a dispersant compares about mutually different samples 18-21. In addition, as mentioned above, in the weight average molecular weight of the denaturation polyacrylic ester used as a dispersant, a difference is between a sample 19 and a sample 20.

[0169] Although any sample of the viscosity in a shear rate 0.1 (s-1) was 1.0 or more Pa-s, viscosity rate of change was less than 50% only about the sample 18.

[0170] By the sample 18, since the dispersant is not included, adsorption to the nickel powder as formed element powder is only a resinous principle. Only by the resinous principle, since adsorption to nickel powder is not enough, viscosity rate of change falls with the condensed nickel powder with a dispersibility fall. Moreover, on the printing paint film, the massive object was checked, with the stacked type ceramic condenser after baking, short [ poor ] occurred frequently and stable quality was not able to be realized.

[0171] Thus, by the sample 18 with low viscosity rate of change, since the fluidity of a conductive paste did not improve at the time of printing, sufficient printing paint film thickness was not obtained according to faults, such as version plugging, and the flake by poor imprint was also generated. Consequently, sufficient electrostatic capacity was not obtained by reduction of the effective area of the inner conductor film.

[0172] Moreover, except for the weight average molecular weight of a dispersant being less than 4500, and weight average molecular weight being 4500 or more by the sample 20, viscosity rate of change was small as compared with the sample 19 of the same conditions. Under the conditions adopted in this experiment, even if it is a sample 20, the printability which is satisfactory practically is acquired, but in order to realize the printability by which high quality was stabilized more, it is desirable that the weight average molecular weight of a dispersant is 4500 or more.

[0173] next -- although samples 22 differ greatly in the point that the "paste manufacture approach" is "1" as compared with the sample mentioned above -- both gravure fitness and the electrical characteristics of a stacked type ceramic condenser -- although -- the result of having excelled is shown.

[0174] Next, samples 23 and 24 are the same presentation systems mutually, and use for and produce "2" as the "paste manufacture approach", using two or more solvent components.

[0175] The solvent component in a sample 23 was the partially aromatic solvent of toluene/terpineol, and it was made to distribute, adding the toluene of an excessive amount to the 1st slurry and the 2nd slurry, and reducing the viscosity of each slurry, and it removed a part for an excess at the 4th process to the design value of toluene after that.

[0176] Moreover, although it was finally the partially aromatic solvent of toluene/terpineol, as mentioned above, the solvent component of a sample 24 added the methanol, and after reducing the viscosity of a slurry and distributing it to the 1st slurry and the 2nd slurry, it removed the whole quantity of the added methanol at the 4th process to them.

[0177] According to these samples 23 and 24, even if it adopts which an above-mentioned approach, it turns out that the result which is satisfactory about the condition of viscosity and a printing paint film and each of electrostatic capacity is obtained.

[0178] Next, samples 25 and 26 are the examples of a comparison which adopted "package mixing" as the "paste manufacture approach", as mentioned above. By these samples 25 and 26, although viscosity rate of change is 50% or more, the viscosity in a shear rate 0.1 (s-1) is less than 1.0 Pa-s.

[0179] According to these samples 25 and 26, since the viscosity in a low shear rate region was low, by the quiescent state, sedimentation of formed element powder, such as nickel powder, took place, and the conductive paste carried out phase splitting. Therefore, dispersion in printing paint film thickness was large, and it was difficult to obtain a normal printing paint film. Consequently, the electrostatic capacity of a design value was not obtained about the electrical characteristics of a stacked type ceramic condenser.

[0180] As mentioned above, although the conductive paste for gravures which uses this invention for formation of the inner conductor film of a stacked type ceramic condenser was explained, the conductive paste for gravures concerning this invention is not limited to such an application, and can be applied also as a conductive paste for forming the inner conductor film with which laminating ceramic electronic parts, such as a

multilayered ceramic substrate, are equipped by gravure.

[0181]

[Effect of the Invention] As mentioned above, according to the conductive paste for gravures concerning this invention Since the viscosity in a shear rate 0.1 (s-1) is the thixotropy fluid of 1 or more Pa-s, and the viscosity rate of change in a shear rate 10 (s-1) is 50% or more when based on the viscosity in a shear rate 0.1 (s-1) Since the viscosity which can prevent sedimentation of the formed element which contains metal powder in the state of a comparatively low shear rate can be held, a viscosity down can be carried out with the comparatively high shear rate which joins a conductive paste at the time of printing and a fluidity can be raised In gravure, the stable continuation printing nature in a high speed can be obtained, it can have good productive efficiency, and laminating ceramic electronic parts like a stacked type ceramic condenser can be manufactured.

[0182] Structure defects by the difference of the contraction behavior of the inner conductor film and a ceramic layer, such as peeling and a crack, can be made hard to produce, when calcinating the raw layered product for laminating ceramic electronic parts, if the formed element contained in a conductive paste contains ceramic powder in this invention.

[0183] In the conductive paste concerning this invention, when the metal powder contained as a formed element is powder containing nickel or base metal like copper, compared with the case where the powder which consists of noble metals is used, the cost of a conductive paste or the cost of laminating ceramic electronic parts can be reduced.

[0184] The condensation based on magnetism etc. can be made hard to produce, for example, if first [ an average of ] particle size of the metal powder contained in a conductive paste is set to 0.05 micrometers or more.

[0185] If first [ an average of ] particle size of the metal powder contained in a conductive paste is set to 0.5 micrometers or less, it can fully respond to the demand of the lamination of the ceramic layer formed along with the lamination of the inner conductor film and the inner conductor film which are formed with this conductive paste.

[0186] It can acquire more certainly adsorbent [ with a sufficient resinous principle / as opposed to / that the weight average molecular weight of the resinous principle contained in a conductive paste is 5000 or more / formed element powder ].

[0187] When the dispersant contained in a conductive paste contains an anionic dispersant and this anionic dispersant is with a weight average molecular weight of 4500 or more polymerization reagent, it can acquire more certainly adsorbent [ of the dispersant to formed element powder / sufficient ].

[0188] According to the manufacture approach of the conductive paste concerning this invention, the 1st mill base containing a formed element, a dispersant, and a solvent component moreover, mixing and by carrying out distributed processing The primary process which obtains the 1st slurry, and by carrying out distributed processing of the 2nd mill base which mixed the resinous principle and the solvent component to the 1st slurry Since it is made to carry out the secondary process which obtains the 2nd slurry, and the 3rd process which removes a massive object 1.0 micrometers or more from the 2nd slurry Since it becomes easy it to become easy for the front face of the formed element powder containing metal powder to make an organic substance component stick to homogeneity efficiently, and to acquire a good distributed condition The characteristic conductive paste concerning this invention that was mentioned above can be manufactured with positive and high productive efficiency.

[0189] If it is made to carry out the 4th process which adjusts the solvent ratio under conductive paste by removing a part of solvent component after the 3rd above-mentioned process further, a superfluous solvent component can be added at the primary process [ 3rd ], therefore hypoviscosity-ization of each mill base will be attained. Therefore, while being able to raise the working efficiency of the massive object removal process carried out at distributed processing carried out at the primary secondary process, or the 3rd process, the effectiveness of these distributed processing and massive object removal can be raised.

[0190] If the viscosity of the 2nd slurry before removing a massive object in the 3rd process is adjusted to 0.5 or less Pa-s, compaction of the time amount which becomes possible [ performing massive object removal efficiently ], therefore is required for massive object removal can be aimed at.

[0191] In the 3rd process, if the filter whose openings are the more than twice of the first [ an average of ] particle size of metal powder and 20 micrometers or less is used, the amount of loss of metal powder can be stopped few, removing a massive object certainly.

[0192] In the 3rd process, if two or more steps of multistage filtration is applied, while being able to develop the life of the filter used, a higher filtration accuracy can be attained.

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[Translation done.]

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**CLAIMS**

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[Claim(s)]

[Claim 1] It is the conductive paste used in order to form said inner conductor film in laminating ceramic electronic parts equipped with the inner conductor film prolonged in accordance with the specific interface between two or more ceramic layers and said ceramic layer by gravure. 30 - 70% of the weight of the formed element containing metal powder, and 1 - 10% of the weight of a resinous principle, When the viscosity in a shear rate 0.1 (s-1) is the thixotropy fluid of 1 or more Pa-s and is based on the viscosity in a shear rate 0.1 (s-1) including 0.05 - 5% of the weight of a dispersant, and the solvent component as the remainder The conductive paste whose viscosity rate of change in a shear rate 10 (s-1) is 50% or more.

[Claim 2] Said formed element is a conductive paste containing ceramic powder according to claim 1.

[Claim 3] Said metal powder is a conductive paste according to claim 1 or 2 which is the powder containing base metal.

[Claim 4] Said base metal is a conductive paste containing nickel or copper according to claim 3.

[Claim 5] The first [ an average of ] particle size of said metal powder is a conductive paste according to claim 1 to 4 which are 0.05 micrometers or more and 0.5 micrometers or less.

[Claim 6] Said resinous principle is a conductive paste according to claim 1 to 5 whose weight average molecular weight is 5000 or more.

[Claim 7] Said dispersant is a conductive paste containing an anionic dispersant according to claim 1 to 6.

[Claim 8] Said anionic dispersant is a conductive paste according to claim 7 the weight average molecular weight of whose it is polymerization reagent and is 4500 or more.

[Claim 9] Said anionic dispersant is a conductive paste containing the monomer which has a carboxylic acid, a sulfonic acid, a phosphoric acid, or the neutralization salt of one of these according to claim 7 or 8.

[Claim 10] The 1st mil base which is the manufacture approach of a conductive paste according to claim 1 to 9, and contains said formed element, said dispersant, and said solvent component mixing and by carrying out distributed processing The primary process which obtains the 1st slurry, and by carrying out distributed processing of the 2nd mil base which mixed said resinous principle and said solvent component to said 1st slurry The manufacture approach of a conductive paste equipped with the secondary process which obtains the 2nd slurry, and the 3rd process which removes a massive object 1.0 micrometers or more from said 2nd slurry.

[Claim 11] The manufacture approach of the conductive paste according to claim 10 further equipped with the 4th process which adjusts the solvent ratio under conductive paste by removing said a part of solvent component after said 3rd process.

[Claim 12] Said 4th process is the manufacture approach of a conductive paste including the process which carries out evaporation removal of said a part of solvent component with the application of either [ at least ] heating or reduced pressure according to claim 11.

[Claim 13] The viscosity of said 2nd slurry before removing said massive object in said 3rd process is the manufacture approach of the conductive paste according to claim 10 or 11 currently adjusted to 0.5 or less Pa-s.

[Claim 14] Said 3rd process is the manufacture approach of a conductive paste including the process from which an opening removes said massive object using the filter which are the more than twice of the first [ an average of ] particle size of said metal powder, and 20 micrometers or less according to claim 10 to 13.

[Claim 15] Said 3rd process is the pressure of 1.5kg/cm<sup>2</sup>. The manufacture approach of a conductive paste including the process which removes said massive object by the pressure filtration of the following according to claim 10 to 14.

[Claim 16] The manufacture approach of a conductive paste according to claim 10 to 15 that two or more steps

of multistage filtration is applied in said 3rd process.

[Claim 17] The manufacture approach of a conductive paste according to claim 10 to 16 that a depth type or surface type filter is used in said 3rd process.

[Claim 18] They are the laminating ceramic electronic parts which consist of a sintered compact which it is laminating ceramic electronic parts equipped with the inner conductor film prolonged in accordance with the specific interface between two or more ceramic layers and said ceramic layer, and said inner conductor film calcinated the conductive paste according to claim 1 to 9, and was obtained.

[Claim 19] Said inner conductor film is laminating ceramic electronic parts according to claim 18 which are equipped with the external electrode electrically connected to the specific thing of said inner conductor film in order to be arranged so that electrostatic capacity may be obtained through said ceramic layer, to be further formed on the outside surface of the layered product constituted with said two or more ceramic layers and to take out said electrostatic capacity, and constitute a stacked type ceramic condenser by it.

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[Translation done.]